1. Introduction

Near ultraviolet (n-UV) based white light-emitting diodes (WLEDs) that are composed of 380–420 nm LED chips and bicolor/tricolor phosphors are emerging as promising high CRI and low CCT lighting sources. Unfortunately, this type of WLED easily suffers from a complicated fabrication process and color unbalance. An available alternative is to develop single-phased white light phosphors. The common single-phased white light infers the energy transfer among activator ion pairs such as Ce³⁺/Eu²⁺– to Mn²⁺, Ce³⁺/Eu²⁺ – to Tb³⁺, Mn²⁺. However, the Mn²⁺ red emission belongs to weak d–d transitions, resulting in the low luminescence efficiency and poor thermal stability. To reduce the energy loss in the energy transfer process, single-activator-doped white light phosphors are highly desired, in which the emission spectra of the single activator must cover the entire visible light range. Eu²⁺ is one of the most popular activators and its 4f–5d transition can be tuned from 400 to 700 nm depending on its coordination environment. Recently, single Eu²⁺-activated materials were designed as single-phased white light phosphors by changing host component, such as Sr₅(PO₄)₃Cl:Eu²⁺. However, to obtain enough full width at half maximum (FWHM) of Eu²⁺ emission is still a challenge. Especially, more red component should be covered for presenting high CRI white light. Eu³⁺-activated materials are potential red-emitting phosphors in pc-WLEDs due to the typical 4f–4f transitions (⁵D₀→⁷F₂, J = 0–6) in the range of 570–700 nm from Eu³⁺. Moreover, cation substitution has been confirmed as an effective strategy to adjust luminescent colors and properties of phosphor materials. In the previous study, we have demonstrated the color-tunable emission from blue or green light to red light based on the valence transformation (3+ to 2+) through cation substitution. However, there are few reports to present single-phased white light emission based on simultaneously blue, green, red-emitting Eu²⁺/Eu³⁺-activated phosphors. Herein, we realize high CRI white lights with low correlated color temperatures by cosubstituting [La³⁺–Si⁴⁺] for [Ca³⁺–P⁵⁺] in the solid solution Ca₈₋ₓLaₓ(PO₄)₆₋ₓ(SiO₄)ₓO₂:Eu²⁺/Eu³⁺.

2. Experimental section

Chemicals and materials

CaCO₃ (Aldrich, ≥99.95%), La₂O₃ (Aldrich, ≥99.99%), SiO₂ (Aldrich, ≥99.99%), (NH₄)₂HPO₄ (Aldrich, ≥99.9%), and Eu₂O₃ (Aldrich, ≥99.99%) were purchased from Sigma-Aldrich Corporation. All of the initial chemicals were used...
without further purification. Aluminum oxide crucibles were used to sinter the phosphor samples.

**Preparation**

A series of Ca$_{8-x}$La$_{2+x}$[(PO$_4$)$_6$-(SiO$_4$)$_x$]O$_2$:2% Eu ($x = 0$–6) compounds were prepared by a conventional high-temperature solid state reaction. The doping concentration of Eu was fixed at 2 atom.% of Ca/La. All samples were synthesized in a reductive atmosphere and Ca$_{8-x}$La$_{2+x}$[(PO$_4$)$_6$-(SiO$_4$)$_x$]O$_2$:2% Eu ($0 \leq x \leq 6$) samples were correspondingly denoted as CLSPO-$x$ ($x = 0$–6). Stoichiometric amounts of CaCO$_3$, La$_2$O$_3$, SiO$_2$, (NH$_4$)$_2$HPO$_4$, and Eu$_2$O$_3$ were thoroughly mixed and pestled in an agate mortar for 1 h. Then, the powder mixtures were placed in aluminum oxides crucibles and sintered in a horizontal tube furnace at 1300 °C for 8 h with a reducing atmosphere of H$_2$ (8%) and N$_2$ (92%) atmosphere. After the furnace slowly cooled to room temperature, the sintered products were ground again, generating the final phosphor powders. The as-prepared Ca$_{8-x}$La$_{2+x}$[(PO$_4$)$_6$-(SiO$_4$)$_x$]O$_2$:2% Eu ($x = 0, 1, 2, 3, 4, 5, 6$) samples were denoted as CLSPO-0, 1, 2, 3, 4, 5, and 6, respectively. Phosphor-converted solid-state lighting devices were fabricated around discrete UV LEDs by using gold wires for electrical operation. The LEDs emit with $\lambda_{\text{max}} = 395$ nm. Homogeneous mixtures of the as-prepared phosphors and transparent silicone resin were cured on the LED chip. After the packaging was completed, the optical properties of the device were measured in an integrating sphere under forward DC bias conditions.

**Characterization**

Finely ground powders were used in all of the measurements. The phase purity of all samples were analyzed using X-ray diffraction (XRD) obtained in a D8 Focus diffractometer (Bruker, Karlsruhe, Germany) at a scanning rate of 1° min$^{-1}$ in the 2θ range from 5° to 120°, and the counting time was 5 s per step with Ni-filtered Cu Kz radiation ($\lambda = 0.15406$ nm). XRD Rietveld profile refinements of the structural models and texture analysis were performed with the use of General Structure Analysis System (GSAS). The photoluminescence measurements were recorded with a Fluoromax-4P spectrophotometer (Horiba Jobin Yvon, New Jersey, USA) equipped with a 450 W xenon lamp as the excitation source. Both excitation and emission spectra were set up to be 1.0 nm with the width of the monochromator slits adjusted as 0.50 nm. XANES of Eu L$_x$ edge was recorded with a wiggler beamline BL17C (the synchrotron X-ray diffraction wavelength $\lambda = 0.774907$ Å) at National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The thermal stability of luminescence of phosphor materials were measured by Fluoromax-4P spectrometer connected a heating equipment (TAP-02). The Commission Internationale de l’Eclairage chromaticity color coordinates, color rendering index ($R_s$), and CCT of WLED devices were measured by Starspec SSP6612.

### 3. Results and discussion

The crystal structure and phase purity of the studied samples were confirmed by powder X-ray diffraction (XRD). Fig. 1a shows the Rietveld XRD refinement of the representative Ca$_{8.88}$La$_{0.92}$Eu$_{0.2}$[(PO$_4$)$_4$-(SiO$_4$)$_2$]O$_2$ (CLPSO-2) sample. The refined structure parameters indicate that the studied sample crystallizes in hexagonal phase with space group $P6_3/m$ (176), $a = b = 9.47$ Å, $c = 6.92$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 538.13$ Å$^3$ and $Z = 1$. The atom positions, fraction factors, and thermal vibration parameters were refined by convergence and satisfied well the refinement conditions, $R_{\text{exp}} = 7.84\%$, $R_p = 4.77\%$, and $\chi^2 = 6.86$. The results imply the formation of single-phased solid solution (CLPSO-2). Fig. 1b shows the XRD patterns for Ca$_{8-x}$La$_{2+x}$[(PO$_4$)$_6$-(SiO$_4$)$_x$]O$_2$:2% Eu ($0 \leq x \leq 6$) samples. Observed and calculated XRD patterns, baseline, and their difference are depicted with black crosses, red solid line, green solid line, and blue solid line, respectively. The short vertical lines show the positions of Bragg reflections of the calculated pattern. (c) A schematic crystal structure and cation-cosubstitution of CLPSO-$x$ along c-axis.
spatial view of the Ca$_{7.84}$La$_{1.96}$Eu$_{0.2}$(PO$_4$)$_6$O$_2$-1350 2% Eu solid solution unit cell is shown in Fig. 1c. Ca/La/Eu occupy the nine-coordinated 4f sites with C$_{3}$ point symmetry and the seven-coordinated 6h sites with C$_{3v}$ point symmetry. Along the c-axis, Ca/LaO$_6$ tetraakisdecahedron chains at 4f sites share faces, while Ca/LaO$_6$ decahedrons at 6h sites share vertexes and edges. The neighbouring tetrakaidecahedron and decahedron are connected through tetrahedral PO$_4$ groups and share edges. With the substitution of Si$_4^+$ for P$_5^+$, the relative Ca$_2^+/La^3+$ ratio will change according to the charge compensation principle, accompanying the site change of the Eu activator at Ca$^{2+}$ and La$^{3+}$ sites.

Fig. 2a and b depict the normalized photoluminescence excitation (PLE) and emission spectra (PL) of CLPSO-x samples prepared at 1300 °C. In previous report, it was found that the PL properties of Ca$_{7.84}$La$_{1.96}$Eu$_{0.2}$(PO$_4$)$_6$O$_2$ phosphors were related to the synthesis temperature. The Eu$^{2+}$ ions in Ca$_{7.84}$La$_{1.96}$Eu$_{0.2}$(PO$_4$)$_6$O$_2$ exhibit blue emission (400–600 nm) and green emission (420–650 nm) when the sintering temperatures are 1250 °C and 1350 °C, respectively. The current CLPSO-0 sample show a broad absorption from 250 nm to 500 nm centered at 395 nm due to the typical 5d–4f transitions of Eu$^{2+}$. Interestingly, under 395 nm UV excitation, it gives a super wide emission band from 420 nm to 700 nm with two emission centers at 467 nm and 556 nm, respectively. Obvi-
ously, this super wide emission band also originates from the 5d–4f transitions of Eu$^{2+}$ ions, and it simultaneously contains the Eu$^{2+}$ emissions of Ca$_{7.84}$La$_{1.96}$Eu$_{0.2}$(PO$_4$)$_6$O$_2$-1250 °C and Ca$_{7.84}$La$_{1.96}$Eu$_{0.2}$(PO$_4$)$_6$O$_2$-1350 °C. The results reveal that two kinds of Eu$^{2+}$ lattice environments appear in CLPSO-0 host at an intermediate sintering temperature (1300 °C). According to the previous conclusions in Eu$^{2+}$-doped (Sr$_{1-x}$Ba$_x$)SiO$_4$N$_2$ system, the super wide Eu$^{2+}$ emission in Ca$_{7.84}$La$_{1.96}$Eu$_{0.2}$(PO$_4$)$_6$O$_2$-1300 °C single-phased sample should be attributed to the nanophase segregation and mixing Ca$_{7.84}$La$_{1.96}$Eu$_{0.2}$(PO$_4$)$_6$O$_2$.

Table 1 CIE color coordinates and emission positions of Ca$_{8-x}$La$_{x}$Al$_{2+y}$PO$_{4-d}$,SiO$_4$O$_2$-2% Eu (CLPSO-x) (0 ≤ x ≤ 6) prepared at 1300 °C, respectively (λ$_{ex}$ = 395 nm)

<table>
<thead>
<tr>
<th>Sample</th>
<th>X</th>
<th>Y</th>
<th>Peak (nm)</th>
</tr>
</thead>
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<tr>
<td>x = 0</td>
<td>0.316</td>
<td>0.386</td>
<td>468</td>
</tr>
<tr>
<td>x = 1</td>
<td>0.322</td>
<td>0.375</td>
<td>540</td>
</tr>
<tr>
<td>x = 2</td>
<td>0.337</td>
<td>0.363</td>
<td>615</td>
</tr>
<tr>
<td>x = 3</td>
<td>0.358</td>
<td>0.358</td>
<td>614</td>
</tr>
<tr>
<td>x = 4</td>
<td>0.423</td>
<td>0.356</td>
<td>614</td>
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</tr>
<tr>
<td>x = 6</td>
<td>0.618</td>
<td>0.383</td>
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single-activator-doped single-phased white light phosphors. The cation-cosubstitution derived.

$\text{Eu}^{2+}/\text{Eu}^{3+}$-tunable strategy could be employed to design the desired single-phased white light in the apatite system.

To further verify the valence transformation of Eu in CLSPO-$x$, a powerful evidence, namely, the normalized Eu L$_3$-edge extended X-ray absorption near edge structure (XANES) spectra of the studied samples were collected in Fig. 4a.$^{26,32}$ Clearly, two peaks at 6975 eV and 6985 eV are observed, which are attributed to the electron transitions of $2p^{3/2}/5d$ in Eu$^{2+}$ and Eu$^{3+}$, respectively.$^{26,32}$ The reason is the bigger shielding effect of nuclear potential by an additional 4f electron in Eu$^{2+}$ than that in Eu$^{3+}$. For the CLSPO-0, Eu almost exists in the form of $2^+$ except for a small amount of residual Eu$^{3+}$, and this finding is consistent with the PL results. Moreover, the obviously higher emission of $^5D_0 \rightarrow ^7F_2$ at 613 nm with respect to the $^5D_0 \rightarrow ^7F_1$ emission at 588 nm indicates that the Eu$^{3+}$ ions mainly enter the deviating inverse symmetry crystalline sites.$^{32,36}$ For the substitution of [Ca$^{2+}$–P$_5^+$] for [La$^{3+}$–Si$^4+$], the absorption intensity of Eu$^{2+}$ systematically increases, while that of Eu$^{3+}$ correspondingly decreases, as shown in Fig. 4a. Finally, the Eu almost evolves to the $3^+$ format $x = 6$. The results convincingly demonstrate that Eu$^{3+}$ and Eu$^{2+}$ could coexist and mutually transform through the cation cosubstitution. A possible transformation mechanism between Eu$^{3+}$ and Eu$^{2+}$ is proposed, as shown by Fig. 4b. In the initial Ca$_8$La$_2$(PO$_4$)$_2$O$_2$ lattices, the Eu ions preferentially occupy the Ca$^{3+}$ (6h) sites, presenting the Eu$^{2+}$ broad band emission. A moderate sintering temperature induces the mixing nanophases of Ca$_4$La$_4$(PO$_4$)$_2$O$_2$ and Ca$_4$La$_4$(SiO$_4$)$_2$O$_2$ in the domain region, which further generates the multi-emitting sites of Eu$^{2+}$ ions and produces a yellow-green emission. With the introduction of Si$^{2+}$, the La$^{3+}$ ions at 6h sites simultaneously enter the Ca$^{2+}$/Eu$^{2+}$ sites to balance charge, and thus Eu$^{2+}$ ions gradually evolve to be Eu$^{3+}$ ions. For the starting structure, the La$^{3+}$ ions occupy all 6h sites and half of 4f sites in the ending Ca$_2$La$_8$(SiO$_4$)$_6$O$_2$ host. Therefore, the Eu$^{3+}$ ions are finally completely transformed to Eu$^{3+}$ ions. In general, the cation cosubstitution strategy could drive the coexistence and adjustment of Eu$^{2+}$/Eu$^{3+}$ in apatite structures, generating the single-phased white light phosphors for n-UV based WLEDs.

As an important index to evaluate the efficiency and stability of pc-WLEDs devices, the thermal quenching behaviour of CLPSO-$x$ samples from room temperature to 573 K was examined and shown in Fig. 5a.$^{37-42}$ Given a non-radiative transition under high working temperature, it is reasonable to observe the progressive emission attenuation of the studied samples.$^{43-47}$ It is noted that the thermal stability of $x = 2$–6 samples are obviously better than that of $x = 0$, 1 samples. Especially, a prominent improvement appears at $x = 2$, which can obtain 56% of the original emission intensity at room temperature. This is mainly because the outside electrons of Eu have a larger shielding effect for the $4f$–$4f$ transitions relative to its $5d$–$4f$ transitions.$^{12,36}$ Therefore, a weak electron-photon coupling interaction occurs and leads to a low thermal quenching under...
high temperature environment. Finally, the x = 0 and x = 2 samples were fabricated to be single-phased white light-emitting devices combined with the 395 nm n-UV chips. Fig. 5b shows the corresponding electroluminescence (EL) spectra of the packaged WLEDs devices under a 200 mA forward bias current, which are basically in agreement with their PL results. Simultaneously, the packaged WLEDs present high $R_a$ and low CCT, namely, $R_a = 95.9$, CCT = 5690 K for x = 0 sample and $R_a = 93.2$, CCT = 3680 K for x = 2 sample, respectively. The CIE color coordinates of x = 0 and 2 samples are calculated to be (0.33, 0.33) and (0.38, 0.34), respectively. Therefore, excellent warm white light with high $R_a$ could be realized in the single Europium-doped apatite phosphor by the cation cosubstitution.

4. Conclusions

In conclusions, a novel Eu-activated single-phased white light phosphor was developed based on the presence of multi-emitting Eu$^{3+}$ and the transformation between Eu$^{2+}$ and Eu$^{3+}$ by cation cosubstitution of [La$^{3+}$-Si$^{4+}$] for [Ca$^{2+}$-P$^{5+}$] in apatite analogue. The XRD patterns demonstrate that the formation of Ca$_{8-x}$La$_{2+x}$[PO$_4$]$_6$:x(SiO$_4$)$_2$:2% Eu solid solutions. Ultra broad Eu$^{2+}$ emission from 420 nm to 600 nm imply the mixing nanophases of Ca$_8$La$_2$Eu[PO$_4$]$_6$:x(SiO$_4$)$_2$:O$_2$ samples at different sintering temperatures. The PL and XANES spectroscopy of Eu L$_3$ edge convincingly confirm the valence transformation from Eu$^{3+}$ to Eu$^{2+}$ by the substitution of [La$^{3+}$-Si$^{4+}$] for [Ca$^{2+}$-P$^{5+}$]. Because of a whole cover across the blue, green emission from Eu$^{2+}$ and red emission from Eu$^{3+}$ in CLSPO phosphors, we obtained high $R_a$ warm white lights (95.9 for $x = 0$; 93.2 for $x = 2$), with the corresponding CCT of 5690 K and 3680 K, respectively. The newly developed single Eu-activated white light phosphors exhibit potential applications in single-phase white emitting n-UV pumped LEDs devices.

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Notes and references


